Prediction of Nonlinear Optical Properties of Organic Materials

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To allow screening of potential nonlinear optical organic compounds, researchers have developed a procedure to predict second- and third-order polarizabilities of organic materials that, within families of compounds, is accurate within 25 percent of the experimental values. This will facilitate nonlinear optical research by limited synthesis of new compounds to those most likely to exhibit appropriate properties. The procedure is as follows:

(a) Using a semi-empirical Hamiltonian (AM1), the polarization of the molecule is calculated in the presence of 252 static fields. AM1 has been chosen because it has a more realistic treatment of the nitro groups in aromatic molecules than other semi-empirical Hamiltonians, such as MNDO. The MOPAC program has been modified to perform these calculations.

(b) The polarization versus static-field information is processed by the HYPER program, developed in-house to generate all required tensor elements using polynomial fits. The polynomial fits are performed from orders 4 to 18, and the numerical uncertainty of the values obtained is used as a measure of the error of the prediction. The advantages of the HYPER program over the procedure implemented in MOPAC are twofold: it estimates the effect of numerical instabilities in the data and calculates terms related through Kleinman symmetry independently, so that adherence to this property may be evaluated.

(c) Two major modifications in the method of calculating hyperpolarizabilities were recently incorporated in the MOPAC program. First, the placement of electric “sparkles” to generate the static fields used by MOPAC has been increased in strength and placed 100 times farther from the molecule. Although the molecules experience the same field strength, the field is more homogeneous, allowing for greater numerical stability in the calculations. It also allows one to conduct calculations on much larger molecules such as C84 and other fullerenes. Secondly, calculations involving more fields have given results where Kleinman symmetry is obeyed for even the smallest elements. While this has little effect in the estimations of molecular beta or gamma, it proves the self-consistency and reliability of the method.

(d) For third-order polarizabilities, a term approximating core effects is added, based on the number and type of atoms present. These core corrections were obtained from empirical fits using published experimental values.

(e) In order to allow comparison of predictions with experimental values, adjustments are made to dynamic fields. In the case of second-order polarizabilities, a “correction equation” has been developed based on p-nitroanaline published measurements. In the case of third-order polarizabilities, the correction used is based on the two-level approximation (ground and one excited state).

(f) Finally, the values are adjusted to account for intermolecular effects—solvent effects, in particular. For second-order polarizabilities, scientists obtained two empirical corrections as a function of the refractive index and the dielectric constant of the solvent based on p-nitroaniline data. For third-order polarizabilities, researchers have used empirical data on benzene.

Although the procedure, as it is, has been proven useful for materials scientists, from a scientific point of view, parts (d) and (e) (i.e., accounting for dispersion and intermolecular effects) need further work. Researchers are currently working on developing a correction for dynamic fields based on the two-level approximation.

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